

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re patent

appln. of : Keith C. Hong, et al.

Appln. No: 10/600,847

Filed: June 20, 2003

For: **ALGAE RESISTANT ROOFING  
GRANULES WITH CONTROLLED  
ALGAEICIDE LEACHING RATES,  
ALGAE RESISTANT SHINGLES, AND  
PROCESS FOR PRODUCING SAME**

Group Art

Unit: 1762

Examiner: Elena Tsoy

Docket No: 008-02

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Mail Stop Amendment  
Commissioner of Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**DECLARATION UNDER RULE 132 (37 C.F.R. § 1.132)**

As an inventor of the subject matter claimed in the above-referenced patent application, I declare the following:

1. My education and experience are as follows: I hold a B.S. degree in Chemistry from Illinois State University, an M.S. degree in Chemistry from the University of Wisconsin and a Ph.D. degree in Materials Science & Engineering from Massachusetts Institute of Technology. Since 1999, I have been employed by CertainTeed Corporation as a chemist in the area of roofing products, including roofing products containing mineral roofing granules.
2. I have reviewed the Examiner's Action mailed August 14, 2006 in the above-identified patent application and United States Patents 3,528,842 ("Skadulis") and 4,378,408 ("Joedicke '408").

3. As the Examiner correctly notes, Joedicke '408 discloses the addition of gas-forming compounds such as hydrogen peroxide and sodium perborate to a coating composition containing a pigment such as titanium dioxide to greatly enhance film opacity and afford significant pigment reductions, particularly titanium dioxide in whites, where the coating composition is intended to be used in coatings on roofing granules, by undergoing chemical and/or thermal decomposition to gaseous products early in the film drying process and resulting in the uniform distribution of microscopic light-scattering microvoids (i.e. gas-forming particles throughout the film). The Examiner also correctly observes that Joedicke discloses that granules may be coated with multiple coats with any desired amount of the coating material and that the gas forming compound may be used in any one or more of the coatings.

4. As presently claimed, the present invention requires that cuprous oxide be included in the coating composition as an algacide. However, when the coating composition is "cured" at an elevated temperature, the cuprous oxide confers a dark brown color on the granules.

For example, color readings were taken for the colored algae-resistant granules produced following the procedure of Example 6 of the application, using a HunterLab XE spectrometer. The results were  $L^*=23.09$ ;  $a^*=4.30$ ; and  $b^*=2.68$ . With an  $L^*$  value of 23.09, these are very dark colored materials, and pigment reduction would not be practical.

5. Commercial algae-resistant granules are typically gray in color, reflecting the use of carbon black in the coating compositions. Material Safety Data Sheets for two typical commercial algae resistant roofing granules are appended hereto as Exhibits A and B, and show the presence of carbon black in each.

Color readings were taken for the commercial algae-resistant granules referenced in the MSDS sheets in Exhibit A and B. The results are as follows:

CertainTeed (Gads Hill GH-71 AR granules):  $L^*=32.1$ ;  $a^*=3.38$ ; and  $b^*=6.69$

3M (Little Rock LR-700 AR granules):  $L^*=35.6$ ;  $a^*=1.93$ ; and  $b^*=5.02$

Based on the  $L^*$  values, these are both very dark granules.

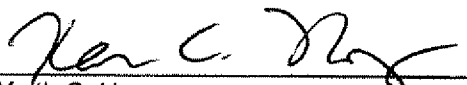
6. One of ordinary skill in the art would not be motivated to add a void-forming material such as hydrogen peroxide or sodium perborate to the inner coating composition material in the process of the present invention, simply because increasing the "opacity" of the coating composition would require additional pigment, rather than less as in the case of white or light-colored materials, and would not improve the appearance of the granules.

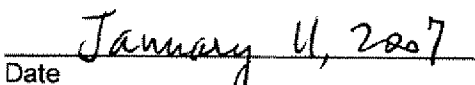
7. With respect to the Examiner's comment in Paragraph 5 of the Examiner's Action that U.S. Patent 4,378,408 ("Joedicke '408") teaches that roofing granules may be coated in multiple coats with any desired amount of coating material and gas-forming compound may be used in any one of multiple coatings to greatly enhance film opacity and afford significant pigment reductions, particularly  $TiO_2$ , in whites (referencing column 5, lines: 38-41), in my opinion one of ordinary skill in this art would have a different understanding of Joedicke '408's teaching. In particular, one of ordinary skill in the art would understand that the effectiveness of microvoids created by gas-forming compounds such as sodium perborate in enhancing the opacity of a multiply layer coating would depend on several parameters, including (1) the specific layer in which the microvoids were created, (2) the composition of the microvoid-carrying layer, (3) the existence of one or more layers exterior to the microvoid-carrying layer and their respective compositions. Thus, while the presence of microvoids in an interior layer coated with a clear, pigment-exterior layer could contribute significantly to the opacity of the entire composition, to the extent the exterior layer or layers includes pigments, the contribution to the opacity of the entire coating composition from microvoids present in interior layers becomes correspondingly less significant. The pigmented outer layer or

layers mask or hide the inner layer, so that light scattering is diminished or extinguished entirely.

8. One of ordinary skill in the art would also understand that while light colored coating compositions may be improved by the presence of microvoids, similar improvement is not to be expected in the case of dark colored coating compositions, which tend to absorb light rather than reflect light. On the contrary, one of ordinary skill in the art would understand the adding light-scattering microvoids to a coating composition having a dark color would tend to work against the colored pigment, by lightening the coating, thus requiring more pigment to achieve a desired color, rather than less as in the case of a light-colored coating composition, such as a white coating composition pigmented with titanium dioxide.

9. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

  
Keith C. Hong

  
Date

# EXHIBIT A

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## \*\*\* 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION \*\*\*

**PRODUCT/TRADE NAME:** Artificially colored mineral roofing granules.

**CAS No:** None

**Common Name** Roofing Shingles

**Product Use:** As algae resistant roofing granules on roofing shingles only

**Manufacturer Information**

CertainTeed Corporation

Phone: 573-223-7554

Rt. 2, Highway 49 N

Piedmont, MO 63957

**Distributor/Contact Information**

Distributor's Product Name: 71 AR Roofing Granules Distributor's Product Code: GH 71 AR

CertainTeed Corporation

Phone: 573-223-7554

Rt. 2, Highway 49 N

Piedmont, MO 63957

## \*\*\* 2 - COMPOSITION/INFORMATION ON INGREDIENTS \*\*\*

CAS #	Component	Percent
Not Available	Rhyolite rock	85.7
<b>The following component is present in Rhyolite Rock:</b>		
14808-60-7	Quartz (crystalline silica)	15-30
<b>The remaining composition is as follows:</b>		
1317-39-1	Copper oxide	3-8
1332-58-7	Kaolin clay	4-6
1344-09-8	Soda glass	2-4
64742-52-5	Naphthenic oil	0-0.9
1308-38-9	Chromium (III) oxide	0-0.9
1314-13-2	Zinc oxide	0-0.9
68187-51-9	Zinc Ferrite	0-0.9
1333-86-4	Carbon black	0-0.9
13463-67-7	Titanium dioxide	0-0.9

**Component Information/Information on Non-Hazardous Components**

**A: General Product Information**

This product is considered hazardous under 29 CFR 1910.1200 (Hazard Communication).

\* Natural Slate granules are a mixture of minerals including quartz.

**B: Component Exposure Limits**

**Quartz (crystalline silica) (14808-60-7)**

ACGIH: 0.05 mg/m3 TWA (respirable fraction)

OSHA: 0.1 mg/m3 TWA (respirable dust)

NIOSH: 0.05 mg/m3 TWA (respirable dust)

**Kaolin clay (1332-58-7)**

ACGIH: 2 mg/m3 TWA (respirable fraction, particulate matter containing no asbestos and < 1% crystalline silica)

OSHA: 10 mg/m3 TWA (total dust); 5 mg/m3 TWA (respirable fraction)

NIOSH: 10 mg/m3 TWA (total dust); 5 mg/m3 TWA (respirable dust)

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## Zinc oxide (1314-13-2)

ACGIH: 2 mg/m3 TWA (respirable fraction)  
10 mg/m3 STEL (respirable fraction)  
OSHA: 5 mg/m3 TWA (fume); 10 mg/m3 TWA (total dust); 5 mg/m3 TWA (respirable fraction)  
10 mg/m3 STEL (fume)  
NIOSH: 5 mg/m3 TWA (dust and fume)  
10 mg/m3 STEL (fume)  
15 mg/m3 Ceiling (dust)

## Carbon black (1333-86-4)

ACGIH: 3.5 mg/m3 TWA  
OSHA: 3.5 mg/m3 TWA  
NIOSH: 3.5 mg/m3 TWA; 0.1 mg/m3 TWA (as PAH, carbon black in presence of polycyclic aromatic hydrocarbons)

## Titanium dioxide (13463-67-7)

ACGIH: 10 mg/m3 TWA  
OSHA: 10 mg/m3 TWA (total dust)

### \*\*\* 3 - HAZARDS IDENTIFICATION \*\*\*

#### Emergency Overview

Product is green, solid granules, typically 0.02 to 0.100 inches in size. Product is an algicide. May cause mechanical eye, respiratory and skin irritation. This product contains a carcinogen.

#### NFPA Ratings: Health: 1 Fire: 0 Reactivity: 0

Hazard Scale: 0 = Minimal 1 = Slight 2 = Moderate 3 = Serious 4 = Severe

#### HMIS Ratings: Health: 1\* Fire: 0 Physical Hazard: 0 Pers. Prot.: gloves and safety glasses with side shields

Hazard Scale: 0 = Minimal 1 = Slight 2 = Moderate 3 = Serious 4 = Severe \* = Chronic hazard

#### Summary:

Material may irritate skin and eyes on contact or respiratory system if dust or fume is inhaled.

#### Routes of Entry:

Inhalation, skin, and eye contact.

#### Acute Inhalation:

Dusts of this product may cause mechanical irritation of the nose, throat, and respiratory tract. Inhalation of dusts of this product may cause metal fume fever, hemolysis of the red blood cells and injury to the liver, lungs, kidneys and pancreas. Inhalation of petroleum distillate vapors can cause drowsiness, headache and nausea. Ingestion may cause vomiting, gastric pain, dizziness, anemia, cramps, convulsions, shock, coma and death.

#### Chronic Inhalation:

Long term exposure to airborne particles may cause lung damage including a risk of cancer. See Section 11: Toxicological Information.

#### Acute Skin Contact:

Contact with the skin may result in mechanical irritation characterized by itching or redness.

#### Chronic Skin Contact:

None identified.

#### Acute Eye Contact:

Contact with the eye may result in mechanical irritation characterized by itching or redness.

#### Chronic Eye Contact:

None identified.

#### Acute Ingestion:

Ingestion of this product is unlikely. However, ingestion of product may produce gastrointestinal irritation and disturbances.

#### Chronic Ingestion:

None identified.

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## Carcinogenicity

### A: General Product Information

The International Agency for Research on Cancer (IARC) has classified crystalline silica as a Group 1 substance, carcinogenic to humans. This classification is based on the findings of laboratory animal studies (inhalation, injection, and implantation) and epidemiology studies that were considered sufficient for carcinogenicity. Several studies have been conducted to determine the risk of cancer to workers exposed to dusts which contain crystalline silica. However, these studies did not consider other factors or elements that workers may be exposed to. Therefore, the causes of the excess deaths due to cancer could not be precisely determined. Further studies are being conducted to determine the risk of cancer when working with crystalline silica products. Excessive exposure to crystalline silica can cause silicosis, a non-cancerous lung disease. Respirable crystalline silica has been classified by the National Toxicology Program (NTP) as a substance which may reasonably be anticipated to be a carcinogen.

### B: Component Carcinogenicity

#### Quartz (crystalline silica) (14808-60-7)

ACGIH: A2 - Suspected Human Carcinogen

NIOSH: potential occupational carcinogen

IARC: Monograph 68, 1997 (inhaled in the form of quartz or cristobalite from occupational sources)  
(Group 1 (carcinogenic to humans))

#### Kaolin clay (1332-58-7)

ACGIH: A4 - Not Classifiable as a Human Carcinogen

#### Carbon black (1333-86-4)

ACGIH: A4 - Not Classifiable as a Human Carcinogen

NIOSH: potential occupational carcinogen (in presence of polycyclic aromatic hydrocarbons)

IARC: Monograph 65, 1996 (Group 2B (possibly carcinogenic to humans))

#### Titanium dioxide (13463-67-7)

ACGIH: A4 - Not Classifiable as a Human Carcinogen

NIOSH: potential occupational carcinogen

IARC: Monograph 47, 1989 (Group 3 (not classifiable))

## Mutagenicity:

None identified.

## Teratogenicity:

None identified.

## Reproductive Toxicity:

None identified.

## Toxicological Synergistic Products:

None identified.

## Medical Conditions Aggravated by Exposure:

Respiratory or skin conditions that are aggravated by mechanical irritants may be at an increased risk for worsening from exposure to dust.

## \*\*\* 4 - FIRST AID MEASURES \*\*\*

### Inhalation:

Remove to fresh air. Drink water to clear throat, and blow nose to remove dust. If symptoms persist, get medical attention.

### Skin:

For skin contact, wash immediately with soap and water. If irritation persists, get medical attention.

### Eyes:

Flush eyes with large amounts of water for 5-15 minutes. If irritation develops, or persists, seek medical attention.

### Ingestion:

Ingestion is unlikely under normal conditions. If granules are swallowed, seek medical attention or advice. Do not induce vomiting.

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## Fires:

Move to fresh air. Administer oxygen and get help.

### \*\*\* 5 - FIRE FIGHTING MEASURES \*\*\*

#### Extinguishing Media:

Use methods for the surrounding fire. Dry chemical, foam and water fog.

#### Special Fire-Fighting Procedures:

Firefighters should wear full protective clothing including self contained breathing apparatus.

#### Hazardous Decomposition Products

Upon decomposition, this product emits carbon monoxide, carbon dioxide and/or low molecular weight hydrocarbons.

Flash Point: Not available

Upper Flammable Limit (UFL): Not determined

Auto Ignition: Not available

Rate of Burning: Not available

Method Used:

Lower Flammable Limit (LFL): Not determined

Flammability Classification: Non-combustible

#### Unusual Fire and Explosion Hazards:

Product contains a small percentage of petroleum distillate that has a flashpoint of 149°F and may be combustible.

### \*\*\* 6 - ACCIDENTAL RELEASE MEASURES \*\*\*

#### Spills:

Pick up large pieces. Scoop up material and put into a suitable container for disposal as a non-hazardous waste.

#### Accidental or Unplanned Releases:

None necessary.

#### Personal Protective Equipment:

See Section 8 of this MSDS for recommended PPE.

### \*\*\* 7 - HANDLING AND STORAGE \*\*\*

#### Handling:

For industrial use only as surfacing of roofing shingles. Avoid generation of dusts. Control dusting with engineering practices or wear personal protective equipment including respirator. Wash thoroughly after handling. Avoid contact with skin and eyes. Use good general housekeeping practices to prevent accumulation of dust in work area.

#### Storage:

Store away from water, oxidizing agents, and acids.

### \*\*\* 8 - EXPOSURE CONTROL / PERSONAL PROTECTION \*\*\*

#### Work Practices and Engineering Controls:

Ventilation should effectively remove and prevent buildup of any vapor/mist/fume/dust generated from the handling of this product.

#### PERSONAL PROTECTIVE EQUIPMENT

##### Eye:

Safety glasses with sideshields.

##### Respirators:

If ventilation is not sufficient to effectively prevent buildup of fumes or dusts, appropriate NIOSH/MSHA respiratory protection must be provided.

##### Skin:

Leather or cotton gloves should be worn to prevent skin contact and irritation. Normal work clothing (long sleeved shirts and long pants) is recommended.

##### Other Protection:

Protective equipment should be provided as necessary to prevent irritation to the throat, eyes, and skin, and to keep exposures below the applicable exposure limits identified in Section 8.

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## \*\*\* 9 - PHYSICAL AND CHEMICAL PROPERTIES \*\*\*

**Appearance:** green  
**Physical State:** solid granules  
**Vapor Pressure:** Not applicable  
**Boiling Point:** Not applicable  
**Solubility (H2O):** Negligible  
**Viscosity:** Not applicable

**Odor:** slightly oily odor  
**pH:** 7.0 - 10.0  
**Vapor Density:** Not applicable  
**Melting Point:** >3000°F  
**Specific Gravity:** 2.5 - 2.8

## \*\*\* 10 - REACTIVITY \*\*\*

### Stability:

This is a stable material.

### Corrosivity:

Not applicable

### Incompatibility:

Strong oxidizing agents, reducing agents, strong acids and alkalies. Hydrofluoric acid will dissolve base rock.

### Reactivity:

Not applicable

### Reactivity with water:

None.

### Hazardous Decomposition Products:

Upon decomposition, this product emits oxides, fumes, and/or low molecular weight hydrocarbons.

### Explosion:

None expected.

### Hazardous Polymerization

Will not occur.

## \*\*\* 11 - TOXICOLOGICAL INFORMATION \*\*\*

Overexposure to dusts may result in pneumoconiosis, a lung disease due to permanent deposition of substantial amounts of particulate matter in the lungs. Chronic inhalation of kaolin dust can cause kaolinosiis, a particular type of pneumoconiosis characterized by positive x-ray findings and mild reductions in pulmonary function. Excessive inhalation of respirable crystalline silica dust may cause a progressive, disabling and sometimes fatal lung disease called silicosis. Symptoms of silicosis include cough, shortness of breath, wheezing, non-specific chest illness and reduced pulmonary function.

### Acute Effects:

#### A: General Product Information

The primary acute health effects of this product include mechanical irritation of the skin, eyes and throat as a result of contact with material.

Copper oxide, a component of this product, may cause metal fume fever, hemolysis of the red blood cells and injury to the liver, lungs, kidneys and pancreas. Ingestion may also cause vomiting, gastric pain, dizziness, anemia, cramps, convulsions, shock, coma and death.

#### B: Component Analysis - LD50/LC50

##### Copper oxide (1317-39-1)

Oral LD50 Rat: 470 mg/kg

##### Zinc oxide (1314-13-2)

Oral LD50 Mouse: 7950 mg/kg

##### Carbon black (1333-86-4)

Oral LD50 Rat: >15400 mg/kg; Dermal LD50 Rabbit: >3 g/kg

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## Chronic Effects:

This product contains crystalline silica. Crystalline silica is considered hazardous by inhalation. Prolonged and repeated inhalation of respirable crystalline silica can cause silicosis, a chronic lung disease characterized by fibrosis and scarring of the lung tissue resulting in a decrease in lung function, breathlessness, wheezing, coughing and sputum production. Short term overexposures to extremely high concentrations of respirable crystalline silica can produce acute silicosis. Acute silicosis is a disease that can rapidly progress within months of initial overexposure and reportedly has caused death within 1 to 2 years.

## \*\*\* 12 - ECOLOGICAL INFORMATION \*\*\*

### Ecotoxicity

#### A: General Product Information

No additional information available.

#### B: Component Analysis - Ecotoxicity - Aquatic Toxicity

No ecotoxicity data are available for this product's components.

### Environmental Fate

No information available.

## \*\*\* 13 - WASTE DISPOSAL CONSIDERATIONS \*\*\*

### US EPA Waste Number & Descriptions

#### A: General Product Information

This product, as supplied, is not regulated as a hazardous waste by the U.S. Environmental Protection Agency (EPA) under Resource Conservation and Recovery Act (RCRA) regulations. Comply with state and local regulations for disposal. If you are unsure of the regulations, contact your local Public Health Department, or the local office of the EPA.

#### B: Component Waste Numbers

No EPA Listed Waste Numbers are being shown for this product's components.

### Disposal Instructions

Dispose of waste material according to Local, State, Federal, and Provincial Environmental Regulations.

## \*\*\* 14 - TRANSPORTATION INFORMATION \*\*\*

### US DOT Information

Shipping Name: Not regulated for transportation.

## \*\*\* 15 - REGULATORY INFORMATION \*\*\*

### US Federal Regulations

#### A: General Product Information

No information available.

#### B: Clean Air Act

This product is not manufactured with, nor does it contain any Class I ozone depleting chemicals as defined by EPA in Title VI of Clean Air Act Amendments of 1990 (40 CFR Part 82-Production Of Stratospheric Ozone).

This product is not subject to Section 112(r) of the Clean Air Act.

#### C: CERCLA

None of the components of this product are listed under CERCLA (40 CFR 302.4) and present in the material at an amount exceeding the Reportable Quantity (RQ).

#### D: SARA Title III Regulations:

None of this product's components are listed under SARA Section 302 (40 CFR 355 Appendix A), and/or SARA Section 313 (40 CFR 372.65).

Acute Health: No Chronic Health: Yes Fire: No Pressure: No Reactive: No

### State Regulations

#### A: General Product Information

Other state regulations may apply. Check individual state requirements.

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## B: Component Analysis - State

The following components appear on one or more of the following state hazardous substances lists:

Component	CAS	CA	MA	MN	NJ	PA	RI
Quartz (crystalline silica)	14808-60-7	No	Yes	Yes	Yes	Yes	No
Kaolin clay	1332-58-7	No	Yes	Yes	No	Yes	Yes
Chromium (III) oxide	1308-38-9	No	Yes	No	Yes	No	No
Zinc oxide	1314-13-2	Yes	Yes	Yes	Yes	Yes	Yes
Carbon black	1333-86-4	Yes	Yes	Yes	Yes	Yes	Yes
Titanium dioxide	13463-67-7	No	Yes	Yes	Yes	Yes	Yes

## C: California Safe Drinking Water and Toxics Enforcement Act (Proposition 65)

The following statement(s) are provided under the California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65):

WARNING! This product contains a chemical known to the state of California to cause cancer.

## Component Analysis - WHMIS IDL

The following components are identified under the Canadian Hazardous Products Act Ingredient Disclosure List:

Component	CAS #	Minimum Concentration
Quartz (crystalline silica)	14808-60-7	1 % (English Item 1406, French Item 1491)
Copper oxide	1317-39-1	1 % (English Item 437, French Item 1307)

## Additional Regulatory Information

### A: General Product Information

No information available.

### B: Component Analysis - Inventory

Component	CAS #	TSCA	DSL	EINECS
Quartz (crystalline silica)	14808-60-7	Yes	Yes	Yes
Copper oxide	1317-39-1	Yes	Yes	Yes
Kaolin clay	1332-58-7	Yes	Yes	No
Soda glass	1344-09-8	Yes	Yes	Yes
Naphthenic oil	64742-52-5	Yes	Yes	Yes
Chromium (III) oxide	1308-38-9	Yes	Yes	Yes
Zinc oxide	1314-13-2	Yes	Yes	Yes
Zinc Ferrite	68187-51-9	Yes	Yes	Yes
Carbon black	1333-86-4	Yes	Yes	Yes
Titanium dioxide	13463-67-7	Yes	Yes	Yes

## \*\*\* 16 - ADDITIONAL COMMENTS \*\*\*

### Other Information

Reasonable care has been taken in the preparation of this information, but the manufacturer makes no warranty of merchantability or any other warranty, expressed or implied, with respect to this information. The manufacturer makes no representations and assumes no liability for any direct, incidental or consequential damages resulting from its use.

### MSDS History

MSDS Revision Summary:

Date:

11/04/2004

MSDS No:

CT10070-1

Comments:

New MSDS

### Key/Legend

CFR = Code of Federal Regulations;

EPA = Environmental Protection Agency;

TSCA = Toxic Substance Control Act;

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ACGIH = American Conference of Governmental Industrial Hygienists;  
IARC = International Agency for Research on Cancer;  
NIOSH = National Institute for Occupational Safety and Health;  
NTP = National Toxicology Program;  
OSHA = Occupational Safety and Health Administration;  
NFPA = National Fire Protection Association;  
HMIS = Hazardous Material Identification System;  
CERCLA = Comprehensive Environmental Response, Compensation and Liability Act;  
SARA = Superfund Amendments and Reauthorization Act;  
DSL = Canadian Domestic Substance List;  
EINECS = European Inventory of New and Existing Chemical Substances;  
RCRA = Resource Conservation and Recovery Act

This is the end of MSDS # CT10070

## **EXHIBIT B**



## Material Safety Data Sheet

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### SECTION 1: PRODUCT AND COMPANY IDENTIFICATION

**PRODUCT NAME:** 3M Brand Copper Roofing Granules - LR7000, LR7022, LR7050 & LR7070 (Little Rock, AR)  
**MANUFACTURER:** 3M  
**DIVISION:** Industrial Mineral Division  
**ADDRESS:** 3M Center  
St. Paul, MN 55144-1000

**EMERGENCY PHONE:** 1-800-364-3577 or (651) 737-6501 (24 hours)

**Issue Date:** 10/04/2006  
**Supersedes Date:** 10/02/2006

**Document Group:** 11-3796-7

#### Product Use:

Intended Use: ROOFING GRANULES FOR ROOFING SHINGLES

### SECTION 2: INGREDIENTS

<u>Ingredient</u>	<u>C.A.S. No.</u>	<u>% by Wt</u>
Nepheline Syenite (composition varies naturally; typically contains feldspars, nepheline, analcite, pyroxene, amphibole, magnetite, and biotite)	68476-25-5	90 - 95
Copper Oxide	1317-39-1	4 - 8
Ceramic Coating	Trade Secret	3 - 7
Inorganic Pigments	Mixture	0.1 - 2
Quartz (a component of Nepheline Syenite)	14808-60-7	< 0.9
Carbon Black	1333-86-4	< 0.5
Chromium (III) Oxide	1308-38-9	< 0.5
Oil	64742-52-5	< 0.5

### SECTION 3: HAZARDS IDENTIFICATION

#### 3.1 EMERGENCY OVERVIEW

**Specific Physical Form:** Granules

**Odor, Color, Grade:** Slightly oily odor, Typical particle size 0.84-2.0 mm

**General Physical Form:** Solid

**Immediate health, physical, and environmental hazards:** Granules are not respirable. Dust generated during handling may contain

respirable material. Contains a chemical or chemicals which can cause cancer.

### 3.2 POTENTIAL HEALTH EFFECTS

**Eye Contact:**

Mechanical eye irritation: Signs/symptoms may include pain, redness, tearing and corneal abrasion.

**Skin Contact:**

Mechanical Skin irritation: Signs/symptoms may include abrasion, redness, pain, and itching.

**Inhalation:**

Upper Respiratory Tract Irritation: Signs/symptoms may include cough, sneezing, nasal discharge, headache, hoarseness, and nose and throat pain.

Prolonged or repeated exposure, above recommended guidelines, may cause:

Silicosis: Signs/symptoms may include breathlessness, weakness, chest pain, persistent cough, increased amounts of sputum, and heart disease.

**Ingestion:**

Gastrointestinal Irritation: Signs/symptoms may include abdominal pain, nausea, diarrhea and vomiting.

**Carcinogenicity:**

Contains a chemical or chemicals which can cause cancer.

<u>Ingredient</u>	<u>C.A.S. No.</u>	<u>Class Description</u>	<u>Regulation</u>
Carbon Black	1333-86-4	Group 2B	International Agency for Research on Cancer
Quartz (a component of Nepheline Syenite)	14808-60-7	Group 1	International Agency for Research on Cancer
Quartz (a component of Nepheline Syenite)	14808-60-7	Known human carcinogen	National Toxicology Program Carcinogens

## SECTION 4: FIRST AID MEASURES

### 4.1 FIRST AID PROCEDURES

The following first aid recommendations are based on an assumption that appropriate personal and industrial hygiene practices are followed.

**Eye Contact:** Flush eyes with large amounts of water. If signs/symptoms persist, get medical attention.

**Skin Contact:** Wash affected area with soap and water. If signs/symptoms develop, get medical attention.

**Inhalation:** Remove person to fresh air. If signs/symptoms develop, get medical attention.

**If Swallowed:** Do not induce vomiting. Give victim two glasses of water. Never give anything by mouth to an unconscious person. Get immediate medical attention.

## SECTION 5: FIRE FIGHTING MEASURES

### 5.1 FLAMMABLE PROPERTIES

Autoignition temperature	<i>Not Applicable</i>
Flash Point	<i>Not Applicable</i>
Flammable Limits - LEL	<i>Not Applicable</i>

Flammable Limits - UEL

*Not Applicable*

## 5.2 EXTINGUISHING MEDIA

Material will not burn.

## 5.3 PROTECTION OF FIRE FIGHTERS

**Special Fire Fighting Procedures:** Wear full protective equipment (Bunker Gear) and a self-contained breathing apparatus (SCBA).

**Unusual Fire and Explosion Hazards:** Not applicable.

Note: See STABILITY AND REACTIVITY (SECTION 10) for hazardous combustion and thermal decomposition information.

## SECTION 6: ACCIDENTAL RELEASE MEASURES

**Accidental Release Measures:** Observe precautions from other sections. Call 3M- HELPS line (1-800-364-3577) for more information on handling and managing the spill. Ventilate the area with fresh air. Reclaim undamaged product. Collect as much of the spilled material as possible. Clean up residue. Place in a closed container approved for transportation by appropriate authorities.

In the event of a release of this material, the user should determine if the release qualifies as reportable according to local, state, and federal regulations.

## SECTION 7: HANDLING AND STORAGE

### 7.1 HANDLING

Do not eat, drink or smoke when using this product. Wash exposed areas thoroughly with soap and water. For industrial or professional use only. Use general dilution ventilation and/or local exhaust ventilation to control airborne exposures to below Occupational Exposure Limits. If ventilation is not adequate, use respiratory protection equipment. 3M does not recommend material handling methods that could damage the coating or base mineral. In particular, roofing granules should not be conveyed pneumatically, via screw conveyors, or used as a sand blasting media. These uses can cause coating and base mineral attrition which may lead to increased levels of dust generation.

### 7.2 STORAGE

Not applicable.

## SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

### 8.1 ENGINEERING CONTROLS

Use with appropriate local exhaust ventilation. Provide local exhaust ventilation at transfer points.

### 8.2 PERSONAL PROTECTIVE EQUIPMENT (PPE)

#### 8.2.1 Eye/Face Protection

The following eye protection(s) are recommended: Safety Glasses with side shields.

#### 8.2.2 Skin Protection

Gloves not normally required. Avoid prolonged or repeated skin contact.

#### 8.2.3 Respiratory Protection

Select one of the following NIOSH approved respirators based on airborne concentration of contaminants and in accordance with OSHA regulations: Half mask R95 particulate respirator, Half mask or full facepiece air-purifying respirator with N100 particulate filters, Half facepiece or fullface air-purifying respirator with P100 particulate filters, Half facepiece or fullface air-purifying respirator with P95 particulate filters, Half facepiece or fullface air-purifying respirator with N95 particulate filters. Consult the current 3M Respiratory Selection Guide for additional information or call 1-800-243-4630 for 3M technical assistance.

#### 8.2.4 Prevention of Swallowing

Do not eat, drink or smoke when using this product. Wash exposed areas thoroughly with soap and water. Wash hands after handling and before eating.

### 8.3 EXPOSURE GUIDELINES

<u><b>Ingredient</b></u>	<u><b>Authority</b></u>	<u><b>Type</b></u>	<u><b>Limit</b></u>	<u><b>Additional Information</b></u>
Carbon Black	ACGIH	TWA	3.5 mg/m3	Table A4
Carbon Black	CMRG	TWA	0.5 mg/m3	
Carbon Black	OSHA	TWA	3.5 mg/m3	Table Z-1
CHROMIUM (III) COMPOUNDS	ACGIH	TWA, as Cr	0.5 mg/m3	Table A4
CHROMIUM (III) COMPOUNDS	OSHA	TWA, as Cr	0.5 mg/m3	Table Z-1
COPPER COMPOUNDS	ACGIH	TWA, as Cu dust or mist	1 mg/m3	
COPPER COMPOUNDS	OSHA	TWA, as dust or mist	1 mg/m3	Table Z-1A
Quartz (a component of Nepheline Syenite)	ACGIH	TWA, respirable	0.025 mg/m3	Table A2
Quartz (a component of Nepheline Syenite)	OSHA	TWA, respirable	0.1 mg/m3	Table Z-1A

#### SOURCE OF EXPOSURE LIMIT DATA:

ACGIH: American Conference of Governmental Industrial Hygienists

CMRG: Chemical Manufacturer Recommended Guideline

OSHA: Occupational Safety and Health Administration

AIHA: American Industrial Hygiene Association Workplace Environmental Exposure Level (WEEL)

## SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

<b>Specific Physical Form:</b>	Granules
<b>Odor, Color, Grade:</b>	Slightly oily odor, Typical particle size 0.84-2.0 mm
<b>General Physical Form:</b>	Solid
<b>Autoignition temperature</b>	<i>Not Applicable</i>
<b>Flash Point</b>	<i>Not Applicable</i>
<b>Flammable Limits - LEL</b>	<i>Not Applicable</i>
<b>Flammable Limits - UEL</b>	<i>Not Applicable</i>
<b>Specific Gravity</b>	2.5 - 2.6 [Ref Std: WATER=1]
<b>Melting point</b>	<i>Not Applicable</i>
<b>Solubility in Water</b>	Negligible
<b>Percent volatile</b>	Nil

## SECTION 10: STABILITY AND REACTIVITY

**Stability:** Stable.

**Materials and Conditions to Avoid:** None known

**Hazardous Polymerization:** Hazardous polymerization will not occur.

### Hazardous Decomposition or By-Products

Substance  
None known.

Condition  
Not Specified

## SECTION 11: TOXICOLOGICAL INFORMATION

Please contact the address listed on the first page of the MSDS for Toxicological Information on this material and/or its components.

## SECTION 12: ECOLOGICAL INFORMATION

### ECOTOXICOLOGICAL INFORMATION

Not determined.

### CHEMICAL FATE INFORMATION

Not determined.

## SECTION 13: DISPOSAL CONSIDERATIONS

**Waste Disposal Method:** Reclaim if feasible. Since regulations vary, consult applicable regulations or authorities before disposal.  
NOTE: Waste is considered a California hazardous waste (See REGULATORY INFORMATION).

**EPA Hazardous Waste Number (RCRA):** Not regulated

Since regulations vary, consult applicable regulations or authorities before disposal.

## SECTION 14: TRANSPORT INFORMATION

### ID Number(s):

98-0111-1209-5, 98-0111-1215-2, 98-0111-1243-4, 98-0111-1255-8, 98-0111-1256-6, 98-0111-1398-6, 98-0111-1512-2, 98-0111-1765-6, 98-0111-1766-4, 98-0111-1767-2, 98-0111-1768-0, 98-0111-1769-8, 98-0111-1770-6, 98-0111-1771-4, 98-0111-1772-2, 98-0111-1797-9, 98-0111-1798-7, 98-0111-1799-5, 98-0111-1800-1, 98-0111-1828-2

Please contact the emergency numbers listed on the first page of the MSDS for Transportation Information for this material.

## SECTION 15: REGULATORY INFORMATION

### US FEDERAL REGULATIONS

Contact 3M for more information.

### 311/312 Hazard Categories:

Fire Hazard - No   Pressure Hazard - No   Reactivity Hazard - No   Immediate Hazard - Yes   Delayed Hazard - Yes

Section 313 Toxic Chemicals subject to the reporting requirements of that section and 40 CFR part 372 (EPCRA):

<u>Ingredient</u>	<u>C.A.S. No</u>	<u>% by Wt</u>
Copper Oxide (COPPER COMPOUNDS (EPCRA 313))	1317-39-1	4 - 8

**FIFRA**

<u>Status</u>	<u>Registration Number</u>
Registered	10350-57

**STATE REGULATIONS**

Contact 3M for more information.

**CALIFORNIA PROPOSITION 65**

<u>Ingredient</u>	<u>C.A.S. No.</u>	<u>Classification</u>
Carbon Black	1333-86-4	**Carcinogen
SILICA, CRYSTALLINE (AIRBORNE PARTICLES OF RESPIRABLE SIZE)	NONE	**Carcinogen

\*\* WARNING: contains a chemical which can cause cancer.

**CHEMICAL INVENTORIES**

The components of this product are in compliance with the chemical notification requirements of TSCA.

Contact 3M for more information.

**INTERNATIONAL REGULATIONS**

Contact 3M for more information.

**ADDITIONAL INFORMATION**

**3M COPPER GRANULES**

Built-in control of algae to maintain the beauty of roofing shingles

**ACTIVE INGREDIENT**

Cuprous oxide 6.0%

**OTHER INGREDIENTS**

Total 94.0%

100.0%

(

**KEEP OUT OF REACH OF CHILDREN**

**CAUTION**

**STORAGE AND DISPOSAL**

Do not contaminate water, food, or feed by storage and disposal.

Pesticide Storage:

Store under ambient conditions.

Pesticide Disposal:

Wastes resulting from the use of this product may be disposed of on-site or at an approved waste disposal facility.

Pesticide Container Disposal:

Return empty container for recycling or reuse.

## DIRECTIONS FOR USE

It is a violation of Federal Law to use this product in a manner inconsistent with its labeling.

If granules are to be stored prior to (and during) use, a copy of this label must be made readily accessible to employees when they are in their work area(s).

3M Copper Granules contain copper oxide, an effective algacide for inhibiting the growth of blue-green algae that can stain roofing shingles. 3M Copper Granules are treated roofing granules 1-2 mm in diameter made from rock coated with copper oxide and sealed in a ceramic shell. The ceramic shell allows a timed release of copper to provide long-lasting algae control that may extend the useful life of shingles.

3M Copper Granules should be mixed with standard roofing granules at the rate of 5-10% by weight and processed normally during manufacture of the shingles.

## WARRANTY

3M warrants that the 3M Copper Granules conforms to the ingredient statement above.

EPA Reg. No. 10350-57

EPA Est. No. 10350-AR-001

EPA Est. No. 10350-WI-002

Net Contents: Bulk shipment; see waybill

3M, St. Paul, MN 55144-1000

## ADDITIONAL INFORMATION

California Code of Regulations (CCR) Title 22 hazardous waste for copper. Empty containers could also be considered hazardous waste and should be disposed of according to state and local regulations.

This MSDS has been prepared to meet the U.S. OSHA Hazard Communication Standard, 29 CFR 1910.1200.

## SECTION 16: OTHER INFORMATION

### NFPA Hazard Classification

Health: 1 Flammability: 0 Reactivity: 0 Special Hazards: None

National Fire Protection Association (NFPA) hazard ratings are designed for use by emergency response personnel to address the hazards that are presented by short-term, acute exposure to a material under conditions of fire, spill, or similar emergencies. Hazard ratings are primarily based on the inherent physical and toxic properties of the material but also include the toxic properties of combustion or decomposition products that are known to be generated in significant quantities.

Revision Changes: Not Applicable

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